Original Article

Acetylene Heterocyclisation Catalysts, Ammonia And Aliphatic Ketones

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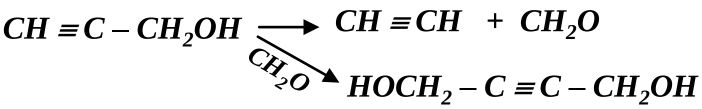
Abstract

The goal is to identify patterns and study the mechanism of synthesis of pyridine bases. The basic principles for the selection and preparation of active and selective catalysts for the synthesis of pyridine bases are proposed. 9 catalytic systems have been developed using oxides of a number of metals of variable valence. The physical and mechanical properties were studied: mechanical strength 37.3-50.2 kg/cm², specific surface area 132.6-278.2 m²/g, porosity 0.31-0.70 cm³/g , bulk density 0.60- 0.93 g/ cm³ ammonia and running time from 51 to 250 hours of the developed catalysts. The adsorption of acetylene on the surface of CA and HXA catalysts has been studied and certain regularities have been determined. **Keywords**: heterocyclization catalysts, acetylene, ammonia, ketones, pyridine bases

Introduction

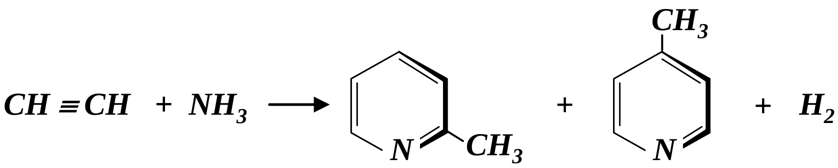
Currently, pyridine bases (PO) are used in agriculture as herbicides of general and selective action, insecticides, fungicides and bactericides [1,2], vitamins and drugs (ftivazide, saluzide, metazid - used in the treatment of tuberculosis diseases) [3], monomers and polymers [4], oil additives and metal corrosion inhibitors [5], suspension stabilizers and extractants [6], dyes and analytical reagents [7]. Preparations such as nitropirine and 2-chloro-6-(trichloromethyl)-pyridine are nitrogen fertilizer stabilizers in the soil. Conducting deep and systematic research on the synthesis of PO undoubtedly makes a significant contribution to the development of a number of sections of organic chemistry and the creation of scientific foundations for organizing the production of pyridine and its derivatives.

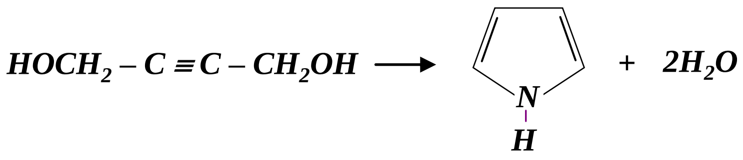
The heterogeneous catalytic synthesis of PO from vinyl acetylene alcohols was further extended to conventional acetylene alcohols [8–10]. Thus, the amination of a mixture of propargyl alcohol with dimethylethynylcarbinol (DMEMK) or its methyl ester in the presence of a CCF catalyst was studied. This results in mixtures of several pyridine derivatives. The implementation of the reaction of propargyl alcohol itself with ammonia leads to the formation, mainly, of 2- and 4-MP, as well as pyrrole. The synthesis of the latter is carried out by catalytic disproportionation at an elevated temperature of the initial alcohol to 1,4-butyndiol [9] and subsequent interaction of this product with ammonia:



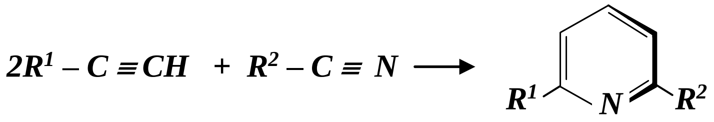
$$CH \equiv C - CH_2OH \longrightarrow CH \equiv CH + CH_2O$$

$$CH \equiv C - CH_2OH \xrightarrow{CH_2O} HOCH_2 - C \equiv C - CH_2OH$$



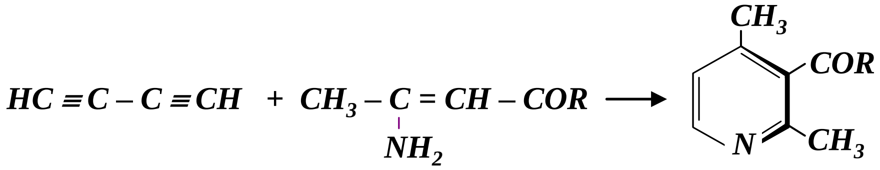


It should be noted that in recent years, along with the above heterogeneous catalytic reactions for obtaining PO from acetylene compounds, much attention has also been paid to the implementation of similar processes in a homogeneous medium. For example, in a number of works [11 - 13], the condensation of acetylenic hydrocarbons with aliphatic nitriles was studied using catalysts - cobalt complex compounds.



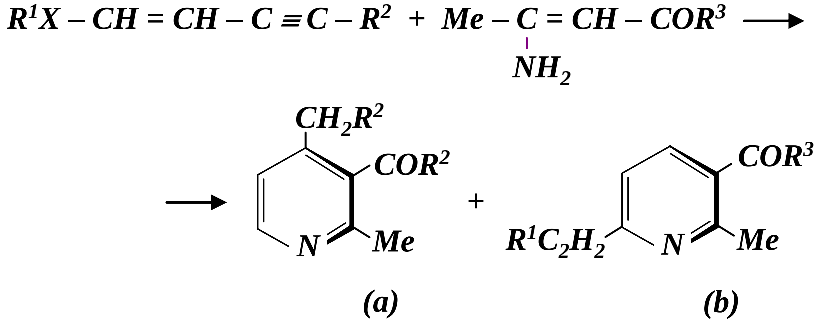
In the reactions carried out, if R1 = H and R2 = -CH3, then 2-MP is obtained as the main product.

In the case of the interaction of diacetylene with ethyl ester of aminocrotonic acid or acetylacetoimine in the presence of equimolar amounts of metallic sodium, ethyl ester of 2,4-dimethylnicotinic acid is synthesized 14]:



where R = Me or OEt.

Petrov A.A. et al. [15] showed that the reaction of 1,3-enyne amines or esters with ethyl ester of β-aminocrotonic acid and acetylacetonylamine leads to the formation of 2,4- and methyl-3-acetylpyridine, as well as esters of 2,4- and 2, 6-dialkyl-3-pyridylcarboxylic acids.

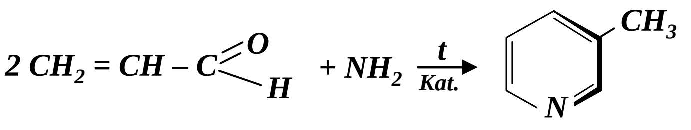
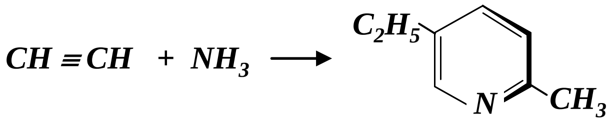
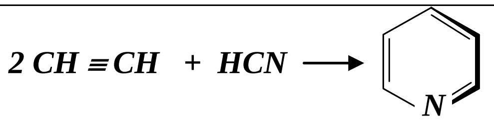
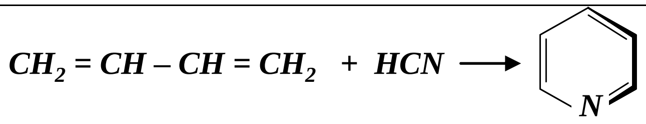
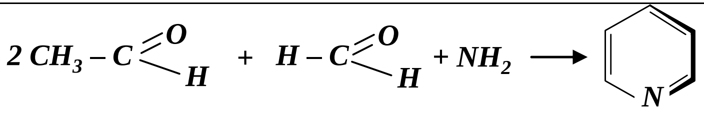
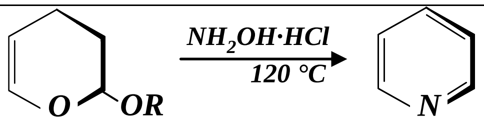


To construct pyridine systems, 1-dialkylamino-1-alkoxy-1-alken-3-ines can also be used as a three-carbon donor. In this case, the two-carbon fragment is supplied by enamines (for example, ethyl ester of a β-aminocrotonic acid), as well as acetylacetonimine or cyanoacetamide [16–18]. The main reaction products are, respectively, 2-methyl-4-alkylnicotinic acid ethyl ester (a) and 2-methyl-6-alkyl-3-acetylpyridines (b): where R3 is OEt (a) or Me (b)

The ratio between the amounts of the formed isomeric esters (a) and (b) of dimethylnicotinic acid was established according to chromatography and PMR spectra, and in both methods the results obtained are in good agreement [16].

At the same time, the synthesis of isomer (a) first involves the addition of a primary amino group at the C(1) electrophilic center, which has a reduced electron density. This nature of the reaction suggests the participation of a free amine function. Indeed, in a number of works [17, 18], the presence of a stable cis-enamine structure of nitrogen-unsubstituted enamino ketones and enamino esters, stabilized by a hydrogen bond between the nitrogen of the amino group and the oxygen of the carbonyl group, was proved. In general, the directed synthesis of a number of pyridine derivatives can be carried out to a certain extent by the methods discussed above. However, due to the difficult accessibility of the starting reagents used, in most cases they represent only a preparative value. Industrial methods for obtaining pyridine bases are shown in table 1 [19 - 23].

Table 1 Industrial methods for the preparation of pyridine bases

Industrial methods for the preparation of pyridine bases Cyclization of acrolein and ammonia	
From acetylene and ammonia	
From acetylene and hydrocyanic acid, the process is catalyzed by mercury(II) chloride	
By the reaction of butadiene with hydrogen cyanide in the presence of aluminum oxide	
By the reaction of thermal cyclocondensation of acetaldehyde, formaldehyde and ammonia at 200 - 250 °C at high pressure on a zeolite catalyst (Chichibabin reaction)	
Action of hydroxylamine on 2-alkoxy-3,4-dihydropyrans	

An analysis of the available literary materials unequivocally indicates the greatest fruitfulness in the preparation of synthetic pyridine bases by the catalytic interaction of carbonyl or acetylene compounds with ammonia and amines. Despite such prospects of these processes, most of them have not yet found proper application. This is due to low yields of target products, ambiguities in the mechanisms of the condensation reactions carried out, low activity and selectivity of the catalysts used, and difficulty in regulating reactions in the desired direction, low availability of initial reagents, etc.

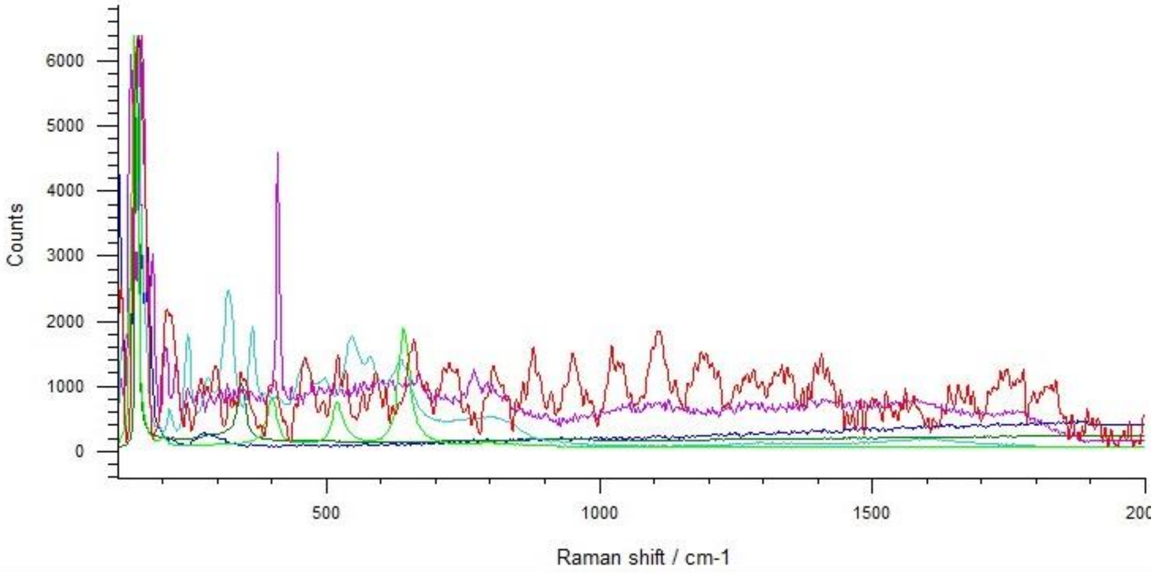
Experimental Part

Preparation of zinc-aluminum catalyst. To 180 g of aluminum hydroxide was added 10.0 g of zinc oxide. In order to increase mechanical strength, as well as create acid sites on the catalyst surface and ensure uniform distribution of components in aluminum hydroxide, 120 ml of a 3–5% hydrofluoric acid solution was added to the resulting mass. The resulting homogeneous mass was molded through a spinneret with a diameter of 4 mm and dried for 3 hours at a temperature of 100 ± 5°C, then calcined at a temperature of 425 ± 25°C with a temperature rise of 50°C per hour and maintaining a temperature of 450 °C within 3 hours. Then the cylinders were cut with a length of 4 mm, sieved from dust. The finished catalyst has a composition, weight%. ZnO - 10.0; Al_2O_3 - 90,0 %.

Results and its discussion

The interaction of acetylene with ammonia in the presence of heterogeneous catalysts at high temperature forms a complex mixture of nitrogen-containing compounds containing 2- and 4-methylpyridines, 2,4- and 2,6-dimethylpyridines, 2,4,6-trimethylpyridine, 2-methyl-5 -ethylpyridine, pyrrole, acetonitrile, dipyridyls, benzene, resin, etc. [24].

In the synthesis of pyridine bases from acetylene, ketones, and ammonia, we used polyfunctional catalysts containing elements of an extremely filled d10 orbital (Zn+2; Cd+2; Cr+3; Ni+2, etc.). Of these, compounds of cadmium and zinc are possible to use in the industrial transformations of acetylene and other organic molecules due to their availability and environmental safety.



Pic.2. ICP Mass Spectral Analysis of HXA Series Catalyst

In the course of studying the promotion of cadmium and zinc compounds by fluorides of some metals and nonmetals and studying the properties of other polyfunctional catalytic systems by X-ray diffraction, it was found that zinc, cadmium, and aluminum fluorides form hydroxyfluorides of the composition Cd(OH)F during catalyst preparation; Zb(OH)F; Cr(OH)2F; Cr(OH)F2; Al(OH)2F; Al(OH)F2, which are probably responsible for the high catalytic activity of the resulting catalysts.

Mass spectrometric ICP MS studies have established that the catalysts have a sufficiently high activity in the semi-amorphous-crystalline state, when chemically bound water is retained. With an increase in the calcination temperature from 450 to 650 C, the proportion of the crystalline phase increases, the amount of chemically bound water decreases, the decomposition of hydroxyfluorides begins, as a result of which the specific surface of the catalyst decreases and its activity decreases.

It has been experimentally found that when the content of zinc and chromium (III) oxides in the composition of catalysts is 3–5 wt %, along with zinc, cadmium and aluminum hydroxyfluorides, the catalysts exhibit sufficient activity and stability in the synthesis of heterocyclic compounds.

It is known in the literature that these elementary steps are catalyzed by compounds of zinc, cadmium, chromium, iron, etc. [25].

In order to search for new stable and highly active catalysts for the heterocyclization of mono- and bifunctional compounds in the vapor phase, we prepared 9 samples of catalysts (Table 3).

Table 3. The composition of the developed catalysts

The initial composition of the mixture of components,g	The composition of the catalyst wt.%	Catalyst symbol
$Cd(NO_3)_3 \cdot 4H_2O$ (24,0 - 36,0) + $Ca(OH)_2$ (153,0 - 164,0) + P_2O_5 (43,0 - 45,0)	CdO (10,0 - 15,0) + CaO (42,0 - 43,0) + P_2O_5 (43,0 - 45,0)	KKF
ZnO (10,0) + $Al(OH)_3$ (134,3)	ZnO (10,0) + $Al(OH)_3$ (90,0)	ЦА
$Ni(NO_3)_2 \cdot 6H_2O$ (11,8) + Cr_2O_3 (3,0) + $Al(OH)_3$ (140,3)	NiO (3,0) + Cr_2O_3 (3,0) + Al_2O_3 (94,0)	HXA- 1
$Ni(NO_3)_2 \cdot 6H_2O$ (19,5) + Cr_2O_3 (3,0) + $Al(OH)_3$ (136,0)	NiO (5,0) + Cr_2O_3 (3,0) + Al_2O_3 (90,0)	HXA- 2
$Ni(NO_3)_2 \cdot 6H_2O$ (27,2) + Cr_2O_3 (3,0) + $Al(OH)_3$ (134,2)	NiO (7,0) + Cr_2O_3 (3,0) + Al_2O_3 (90,0)	HXA- 3
$Ni(NO_3)_2 \cdot 6H_2O$ (35,0) + Cr_2O_3 (3,0) + $Al(OH)_3$ (131,3)	NiO (9,0) + Cr_2O_3 (3,0) + Al_2O_3 (88,0)	HXA- 4
$Ni(NO_3)_2 \cdot 6H_2O$ (42,8) + Cr_2O_3 (3,0) + $Al(OH)_3$ (128,3)	NiO (11,0) + Cr_2O_3 (3,0) + Al_2O_3 (86,0)	HXA- 5
$Ni(NO_3)_2 \cdot 6H_2O$ (50,6) + Cr_2O_3 (3,0) + $Al(OH)_3$ (125,3)	NiO (13,0) + Cr_2O_3 (3,0) + Al_2O_3 (84,0)	HXA- 6

Ni(NO$_3$)$_2$·6H$_2$O (58,4) + Cr$_2$O$_3$ (3,0) + Al(OH)$_3$ (122,3)	NiO (15,0) + Cr$_2$O$_3$ (3,0) + Al$_2$O$_3$ (83,0)	НХА- 7

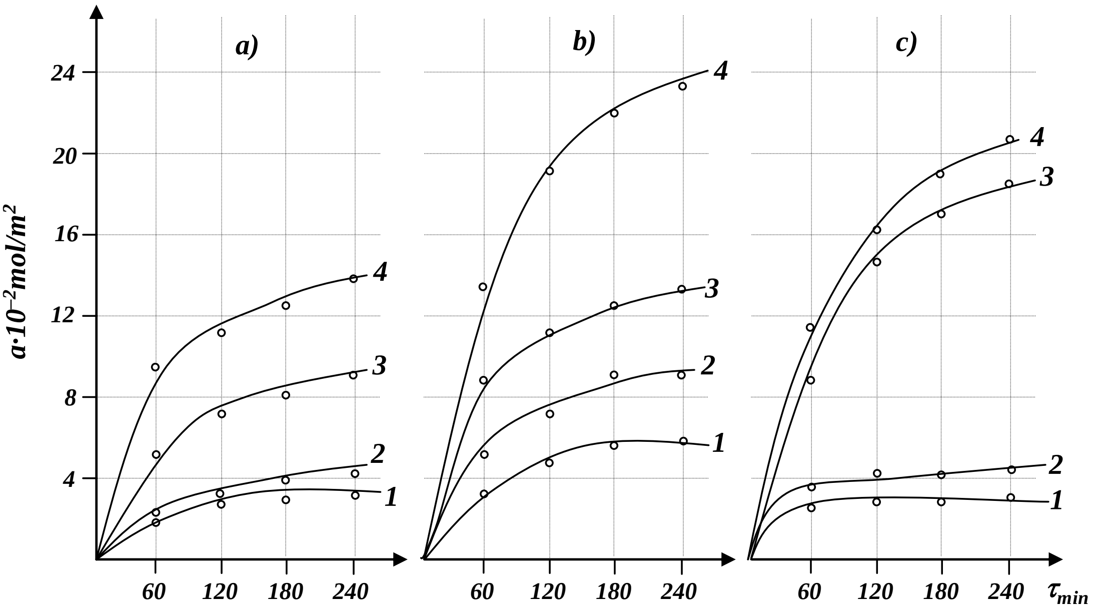
For each prepared catalyst, the mechanical strength, specific surface area, porosity, bulk density, and duration of operation under the conditions of the reactions carried out (until the first regeneration) were found. All results obtained are summarized in Table 4.

Table4 Some characteristic properties of the developed catalysts

Catalyst symbols	Mechanical strength, kg/cm²	Specific surface, m²/g г	Porosity, cm³ /g	Bulk weight, g/cm³	Duration of work before regeneration, hour
ККФ	44,0	132	0,38	0,93	250
ЦА	37,3	140	0,31	0,60	51
НХА-1	41,4	278,0	0,71	0,72	127
НХА-2	41,9	275,2	0,70	0,75	133
НХА-3	46,4	274,4	0,67	0,78	129
НХА-4	47,1	264,1	0,64	0,79	146
НХА-5	48,6	250,0	0,63	0,85	142
НХА-6	49,3	237,2	0,59	0,90	140
НХА-7	50,2	235,1	0,57	0,92	145

As can be seen from the data in this table, depending on the quantitative and qualitative composition of the catalysts, their mechanical strength is in the range of 37.3 - 50.2 kg / cm², specific surface 132.0 - 278.0 m² / g, porosity 0.31 - 0.70 cm³ / g, bulk density 0.60 - 0.93 g / cm³ and the duration of work before regeneration 51 - 240 hours.

As follows from the literature data, basically, studies have been carried out on the adsorption of acetylene only on the surface of metals, graphite, and some compositions from them. However, such studies using catalysts based on various metal compounds have so far remained almost unexplored.



Pic.2 Kinetics of acetylene adsorption on НХА-1 (a), НХА-3 (b), and НХА-5 (c) catalysts at temperatures, °C: 1-150, 2-200, 3-250 and 4-300

Based on the foregoing, in this work, the adsorption of acetylene and ammonia (the main initial reagents in the synthesis of

PO) on the surface of a number of developed systems (Fig. 2). At the same time, adsorption experiments were carried out in the pre-catalytic temperature ranges (150 - 300 °C), the pressure of the tested gases was 28.0□103 Pa (210 mm Hg) and the duration of the experiments was up to 240 minutes.

Yes, on pic.2 the results of studying the kinetics of acetylene adsorption on НХА-1, НХА-3 and НХА-5 catalysts are presented. As follows from them, for all catalysts of the NXA series, the form of kinetic curves is close to each other, i.e. At first, the adsorption of acetylene proceeds at an increased rate, and then it slows down somewhat. This regularity is obviously due to the fact that, with the duration of the experiments up to 60 min, the most active centers are involved in the process, and later also individual less active centers of the catalyst surface.

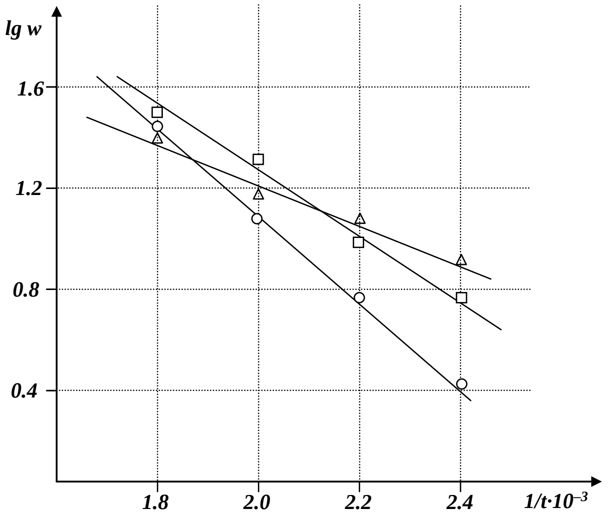
The temperature at which the experiments were carried out also has a significant effect on the adsorption capacity of the catalysts used. For example, in the case of using the HXA-1 catalyst with a run time of 120 min. and temperatures of 150, 200, 250 and 300 °C, the adsorption value of acetylene is 3.8, respectively; 4.2; 7.1 and 11.7.10 mmol/m (Fig. 3a). A similar character is also observed when studying the effect of temperature on the adsorption capacity of other tested catalysts. Apparently, this pattern is mainly explained by the participation of active sites of catalysts at the beginning of the process, and then by the involvement in adsorption of centers activated under the action of additional energy supplied from outside.

The adsorbability of acetylene also largely depends on the composition of the catalysts used. For example, in 120 min at 300°C, 11.5; 17.7 and 15.8 mmol/m² of acetylene, respectively. In general, these catalysts are arranged in a row according to their adsorption capacity: HXA-1 < HXA-5 < HXA-3 i.e. with an increase in the content of nickel oxide in them, the adsorption of acetylene passes through a maximum. It should be noted that an identical pattern also takes place in the case of adsorption of acetylene on a number of catalysts used in the hydrofluorination of acetylene [28].

Thus, the change in the adsorption value with increasing temperature in all cases obeys the well-known Arrhenius equation. The values of the total activation energy of chemisorption of acetylene (Eac) on HXA-1, HXA-3, HXA-5 catalysts were calculated from tgα of the slope of the constructed straight lines, which are respectively equal to 24.8; 30.6; 21.0 kJ/mol. These values of EAC generally correlate with the already established physicochemical properties of the tested catalysts and the revealed kinetic regularities of acetylene adsorption on them. Moreover, earlier a number of authors [28] also found that for the adsorption of acetylene on some other multicomponent catalysts based on γ-Al2O3, the Eac value is in the range of 23.5–27.2 kJ/mol, which is close to the above data.

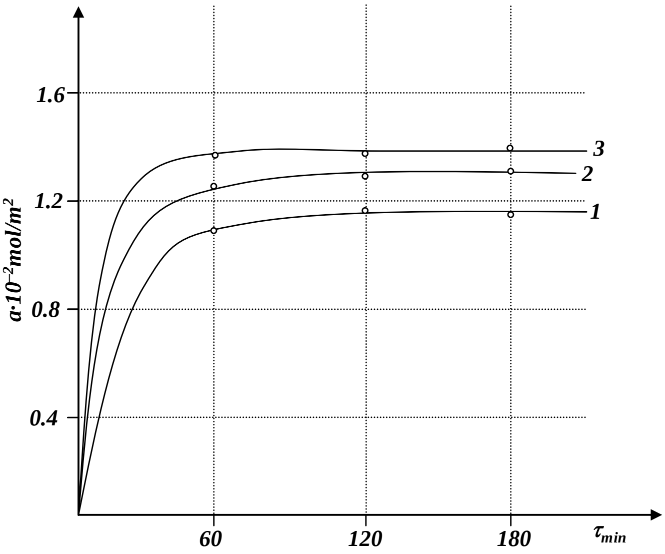
In recent years, some attention has also been paid to the study of ammonia adsorption on catalysts used in heterogeneous catalytic reactions of PO synthesis [29]. So, Uevv A. and others carried out the adsorption of ammonia in a wide range of temperatures on alumina and a sample modified by treatment with hydrofluoric acid. It is shown that in this case the process proceeds on the acid sites of the surface of the applied contacts and the adsorption of ammonia is much greater on the fluorinated catalyst compared to the initial sample.

As an example, Figure 3 shows the data on the kinetics of ammonia adsorption on one of the active catalysts, HXA-3. The experiments were carried out at temperatures of 150, 200, and 300°C. It follows from them that the adsorption of ammonia mainly occurs within 60 min. Then its value almost does not change, i.e. further on the kinetic curves there appear saturation regions, the appearance of which, obviously, is due to the complete filling of individual active centers of the catalyst surface, responsible for the adsorption of ammonia at the corresponding temperatures.



Pic.3. Dependence of lgW on 1/T in the process of acetylene adsorption on HXA series catalysts: l - HXA-1, 2 - HXA-3 and 3 - HXA-5

From the dependence of lgW on 1/t (Fig. 3), the activation energy of ammonia adsorption (Eam) was found, which is equal to 12.6 kJ/mol, i.e. its value also turned out to be lower than the Eac value (30.6 kJ/mol) on the same catalyst.



Pic.4 Kinetics of ammonia adsorption on HXA-3 catalyst at temperatures, °C: 1-150, 2-200 and 3-300

Comparison of ammonia adsorption values, for example, at 150, 200 and 300 °C in 60 min. with some similar data for the adsorption of acetylene (Fig. 2b) shows that in the first case these values are respectively 5 - 10 times less than in the second.

This difference, to a certain extent, indicates a higher proportion of acetylene participation in the formation of PO than ammonia.

As already noted, in previous studies by T.S. Sirlibaev [30, 31] studied in detail the adsorption of acetylene on a number of multicomponent catalysts consisting of γ-Al2O3, AlF3, CdO, Cd(BF4)2, Fe2O3, etc. They turned out to be quite active and selective in the gas-phase hydrofluorination of acetylene, fluorination of vinyl chloride; and dehydrofluorination of 1,1-difluoroethane. In this case, the obtained data on the synthesis of vinyl fluoride correlate to a certain extent with the results of studying the chemical adsorption of acetylene. A similar relationship between the adsorption value of the initial reagents, and also, in some cases, of the target products on the catalysts used and the efficiency of the latter in various reactions, was also revealed in [28].

All of the above, to a certain extent, contributes to a scientifically based explanation of certain regularities in the processes of obtaining software.

Based on the foregoing and combining them with the results of the experiments obtained in this work, it can be argued to a certain extent that, in general, the obtained data on adsorption contribute to the development of a science-based approach in the selection of multicomponent contacts for the synthesis of PO and allow one to pre-determine the optimal conditions for the ongoing reactions. In addition, they also make it possible to suggest the most probable mechanisms of the carried out heterogeneous catalytic interactions of acetylene with ammonia.

Conclusion

The basic principles for the selection and preparation of active and selective catalysts for the synthesis of pyridine bases are proposed. Nine catalytic systems have been developed using oxides of a number of metals of variable valence.

The physical and mechanical properties were studied: mechanical strength 37.3-50.2 kg/cm², specific surface area 132.6-278.2 m²/g, porosity 0.31-0.70 cm³ /g, bulk density 0.60- 0.93 g/cm³ and running time from 51 to 250 hours of the developed catalysts. The adsorption of acetylene on the surface of CA and HXA catalysts has been studied and certain regularities have been determined.

On the whole, the conducted studies made it possible to elucidate some features of the adsorption of acetylene and ammonia on a number of developed catalysts. In particular, characteristic signs of the onset of chemisorption of these gaseous substances in the precatalytic temperature range turned out to be a symbatic increase in the amount of adsorbent with an increase in temperature and a sharp decrease in the rate of the process with time. The shape of the kinetic curves is similar in all cases, and there are no anomalous deviations from the usual. This probably indicates sufficient stability of both acetylene and ammonia under experimental conditions, i.e. the absence of any decomposition of their molecules.

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